



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Generation of an amorphous graphite substrate by cumulative deuterium bombardment with full non-bonded interactions

J. Marian

January 12, 2011

Journal of APplied Physics

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Generation of an amorphous graphite substrate by cumulative deuterium bombardment with full non-bonded interactions

Jaime Marian

*Lawrence Livermore National Laboratory
Livermore, CA 94551*

Abstract: A deuterated amorphous carbon target is generated from a fresh graphite layer by hyperthermal irradiation with deuterium ions using molecular dynamics (MD) simulations. We use interatomic potentials that include non-bonded (long-range) interactions for maximum accuracy and simulate cumulative bombardment up to doses of 5.80×10^{16} ions cm^{-2} at 1000K. The graphite target goes through several stages of erosion and swelling leading to complete amorphization and significant density loss. The calculations show a transition from graphite-like hybridization to a mixture of diamond-like and linear hybridizations with dose. It is concluded that the current sample sizes obtained directly by cumulative irradiation affordable with MD are not sufficiently large to be used for sputtering calculations under steady-state conditions.

1. INTRODUCTION

Fusion energy promises to be a clean, inexhaustible and economical source of energy for the future [1]. However, many technological and scientific challenges still remain, mostly associated with materials performance under harsh operating conditions such as high thermal load, high temperature and high irradiation dose and energy. Under high fluences of 14 MeV neutrons, fusion structural materials will suffer significant radiation damage, changes of physical properties, contamination by tritium, and activation. Plasma-facing materials in magnetic fusion energy devices are subject to an additional type of damage by ELM (edge localized modes), *i.e.* sporadic, very intense, low-energy ion discharges that result in irreversible alterations of the surface structure of plasma-facing components (PFC). Some of the most critical plasma-surface interactions (PSI) issues are: (i) the net erosion of PFC, (ii) net tritium retention in surfaces, (iii) fuel and material mixing in the walls,

leading to amorphization, blistering, etc., and (iv) plasma contamination with redistributed impurities, leading to a decreased device performance efficiency [2]. Materials that combine high refractoriness (for high-temperature resistance), low atomic number (for plasma contamination) and acceptable degassing behavior (for tritium retention) are preferred candidates as PFC. Although carbon-based materials such as graphite display good performance in terms of points (i), (iii), and (iv) above, high tritium affinity and little progress in the area of tritium removal has prompted interest in metallic materials such as beryllium and tungsten alloys [3]. In graphite, erosion occurs via different sputtering phenomena, such as physical sputtering of single C atoms [4,5], irradiation-induced release of unsaturated hydrocarbons [6,7], and chemical sputtering [8,9], each one with its own temporal, energy, and angular spectral signatures. In particular, the first two processes are amenable to simulation by atomistic methods, as they typically occur over time scales of the order of <10 ps. Before steady-state sputtering occurs, however, a superficial amorphous layer with a thickness of several microns develops due to prolonged exposure to plasma ions, referred to as “*a*-C:H” layer (or *a*-C:D if deuterium, instead of hydrogen, is considered). This layer typically develops some microstructure associated with the amorphization process, such as surface roughness, voids, blisters, etc. Therefore, suitable *a*-C:H targets must be generated atomistically before conducting molecular dynamics (MD) simulations of carbon sputtering.

a-C:H substrates can either be generated by melting and quenching of mixtures of H and C in the correct proportions (30~40% at. H) [10-12], or by cumulative deposition of low-energy particles on C surfaces, often pre-loaded with some amount of H [13]. The former, termed *unsaturated*, have been shown to possibly underestimate the amount of C sputtering under H/D irradiation tests. However, they possess the advantage that they can be acceptably modeled with short-range potentials for computational efficiency.

Other works have focused on direct bombardment of graphite surfaces, which requires considering non-covalent interactions between the constitutive graphene sheets. These occur over longer distances than covalent C-C bonds, which

increases the computational overhead of the calculations several-fold but is important to capture the cohesive nature of crystalline graphite. Despite this, the great majority of calculations on fresh graphite targets use only short-range potentials [14,15], with one notable exception up to a dose of 1.6×10^{16} ions cm^{-2} . [15]. Here, we explore the direct approach, *i.e.* generating an α -C:D layer by cumulative deposition of D atoms on a crystalline graphite substrate using the full AIREBO potential [16] with short-range corrections [17], which is able to treat both covalent and non-covalent interactions in hydrocarbon systems.

2. RESULTS

2.1. Computational Model

Our target is constructed by rotating a bulk graphite sample by 30° with respect to the nominal hexagonal basal orientation [18]. The target is then cut into a $34.1 \times 19.7 \times 39.0 \text{ \AA}^3$ crystallite containing 2032 atoms, and equilibrated for 500 ps at 1000K using a Langevin thermostat to prepare it for bombardment. This construction effectively generates a $[01\bar{1}1]$ surface, which is the one exposed to the D ions. Periodic boundary conditions are used along the two directions orthogonal to the surface. **Figure 1** shows the initial relaxed graphite crystallite at 1000K. We have chosen to rotate the sample to add variability to the modeling and differentiate it from other similar works in the literature [15].

Each collision event was modeled for 1.5 ps without any temperature control (which typically results in temperature spikes of the order of 100K in the total system), followed by a 5.0-ps annealing again at 1000K before the next collision event occurs. Strictly speaking, this corresponds to a particle flux of $2.3 \times 10^{24} \text{ cm}^{-2} \text{ s}^{-1}$, clearly only attainable during ELM, although the target can be considered fully thermalized after the simulated annealing phase and therefore our results can be considered dose-rate independent. The D-ion velocities, v , are sampled from a hyperthermal Maxwell-Boltzmann distribution at a temperature of $kT \approx 25 \text{ eV}$, compared to temperatures of $\sim 1 \text{ eV}$ roughly to be expected in the plasma edge

region near the divertor [19] (although, discharges of up to keV have been measured during ELMs):

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$$

where m is the deuterium mass and k is Boltzmann's constant. The angle of incidence is sampled uniformly in the $\left[0, \frac{\pi}{2}\right)$ interval; the impinging location is also chosen randomly from the exposed surface. A total of 3900 impacts were simulated corresponding to a total dose of 5.8×10^{16} ions cm^{-2} .

2.2. Graphite target evolution

Figure 2 shows the evolution of the deuterium content in the graphite sample as a function of dose. The absorption efficiency, η , defined as the instantaneous ratio between the number of D ions absorbed relative to the total number of bombarded ions, is also shown. The number of absorbed D ions grows steadily up to a dose of 1.3×10^{16} ions cm^{-2} (≈ 900 impingements) with η in excess of 50%. Thereafter, the efficiency gradually declines to zero at a dose of 2.2×10^{16} ions cm^{-2} (≈ 1600 impingements), signaling temporary saturation. Thence the substrate undergoes a period of high absorption between 2.8 and 4.1×10^{16} ions cm^{-2} (2000 to 2800 impingements), followed by a stage of deuterium emission ($\eta < 0$) before a steady state is reached. However, it is more informative to plot the $\left(\frac{D}{C+D}\right)$ ratio as a function of dose, as this parameter contains information about the collective behavior of the α -C:D target. Consistent with experimental measurements [20], this ratio is seen to saturate at 30% after a dose of 4.8×10^{16} ions cm^{-2} , where the efficiency is still negative before it reaches zero. This implies that the D ions emitted during the periods of $\eta < 0$ do so associated with C atoms from the substrate, which occurs in the form of large unsaturated C_xD_y complexes much in the manner observed by Stuart *et al.* [15].

To measure the degree of amorphization of the graphite substrate, we calculate the pair correlation function $g(r)$ and plot it in **Figure 3**. The figure shows the C-C pair correlation function for the pure graphite system of Fig. 1, as well as for after the last of the 3900 deuterium impacts (maximum dose). For comparison, we have also added the $g_{C-C}(r)$ for the α -C:D substrate generated via melting plus quenching, which was used for the study in ref. [7]. We refer to the former as *saturated* α -C:D, in contrast to the one used in [7] (unsaturated). Several observations are worth being remarked. First, the atomic density of both amorphous samples is very similar and about eight times lower than that of pure graphite ($\approx 2.1 \text{ g cm}^{-3}$). As we shall see, this is consistent with the formation of large cavities in the saturated α -C:D target associated with periods of negative η in Fig. 2. Second, although both the saturated and unsaturated samples contain no structure beyond the second nearest-neighbor shell, the magnitude of the peaks in the former is less pronounced. The final configuration can be seen in **Figure 4**, where no trace of crystal order remains. Relatively large amounts of open volume can be seen, surrounded by highly disordered C-H regions, including long unsaturated C chains.

The total pair correlation function including D-C (and C-D) correlations is shown in **Figure 5** as a function of dose. Two dilation transitions (density decrease) can be clearly recognized in the figure: one from 1.93 to $2.97 \times 10^{16} \text{ ions cm}^{-2}$, and another from 4.46 to $5.80 \times 10^{16} \text{ ions cm}^{-2}$. These again correspond to periods of negative absorption coefficient in Fig. 2. A similar process was observed by Stuart *et al.* in their AIREBO calculations of [0001] graphite [15]. However, on the basis of the shape of $g_t(r)$, it is seen that, qualitatively, the system can be considered amorphized after a dose of roughly $3.50 \times 10^{16} \text{ ions cm}^{-2}$, and that, what takes place afterwards, are simply emissions of ‘large’ D-C complexes that lower the internal energy of the system. In other words, amorphicity is achieved well in advance of *steady-state*, understood as a dose-independent D/(D+C) ratio. To prepare an α -C:H surface for sputtering simulations amorphization is required, but if not sufficiently equilibrated the target will continue to evolve under subsequent bombardments until steady state is reached.

However, as Fig. 4 shows, in these small cells, steady state is only reached at a dose level that causes the substrate to develop large free volume fractions and what may be identified as some degree of surface roughness, *i.e.* without retaining any sense of underlying ‘bulk’. This would likely result in bogus sputtering yields unless a substrate of fully-dense α -C:D existed underneath to act as a ‘reservoir’ of C atoms.

2.3. Bond hybridization evolution

Another valuable parameter related to the pair correlation function is the sp^3/sp^2 hybridization ratio, which measures the proportion of diamond-like bonds relative to graphite-like bonds. Here we use the same method as Zhong *et al.* [21] to measure the hybridization ratio. The evolution with dose is given in **Figure 6**, where periods of rapid growth and stagnation can be seen to coincide with the evolution displayed by the absorption in Fig. 2. These ratios are in general agreement with experimental [22,23] and simulation [24,25] values. However, what is striking is the large amount of linear configurations (sp^1) found, also plotted in Fig. 6, which are typically rare in carbon solids.

3. DISCUSSION AND SUMMARY

As noted by Krstic and Reinhold [26], cumulative bombardment not only erodes the surface, but also creates surface swelling producing a lower-density interface that is inhomogeneous and contains filamentous structures of hydrocarbon chains, which play an important role in the PSI dynamics. This entirely consistent with the present simulations, even though the target preparation method and interatomic potential used by Krstic and Reinhold were different to those employed here. In any case, in the opinion of the author, the morphology and density of the substrate make it unsuitable for recurring sputtering simulations. To ascertain whether the present simulations are representative of graphite thin layers under cumulative bombardment, or just one extreme manifestation of it, one could perform a series of calculations exploring some fraction of the parametric space, *e.g.* the original crystal

orientation, incident energy, simulation temperature, etc., and obtain suitable averages with which to embark oneself in sputtering calculations, which typically necessitate of several thousands of impacts to amass sufficient statistics. However, at present this is unfeasible with available computational resources.

Therefore, we must conclude that the samples that we can currently simulate with state-of-the-art computing and MD implementations are not sufficiently large to produce acceptable α -C:D from fresh graphite targets, at least when considering full nonbonded interactions. What it is shown, however, is that it is possible with MD to reach doses capable of achieving steady-state conditions in α -C:D with AIREBO potentials.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References:

- [1] http://www.firstscience.com/home/articles/big-theories/nuclear-fusion-energy-for-the-future_17006.html
- [2] P. C. Stangeby, "The Plasma Boundary of Magnetic Fusion Devices" (Taylor & Francis, 2000).
- [3] J. Roth, "Review and Status of Physical Sputtering and Chemical Erosion of Plasma Facing Materials" *Springer Series in Chemical Physics*, 2005, Vol. **78**, Part III, 203.
- [4] C. H. Wu, *Journal of Nuclear Materials* **160** (1988) 103.
- [5] J. Küppers, *Surface Science Reports* **22** (1995) 249.
- [6] K. Nordlund, E. Salonen, A. V. Krasheninnikov, and J. Keinonen, *Pure Appl. Chem.* **78** (2006) 1203.
- [7] J. Marian L. A. Zepeda-Ruiz, N. Couto, E. M. Bringa, G. H. Gilmer, P. C. Stangeby, T. D. Rognlien, *Journal of Applied Physics* **101** (2007) 044506
- [8] Ch. Hopf, A. von Keudell, and W. Jacob, *J. Appl. Phys.* **94** (2003) 2373.
- [9] M. Balden, J. Roth, *J. Nucl. Mater.* **280** (2000) 39.
- [10] G. Jungnickel, Th. Frauenheim, D. Porezag, P. Blaudeck, U. Stephan, R. J. Newport, *Phys. Rev. B* **50** (1994) 6709.
- [11] P. S. Krstic, C. O. Reinhold, and S. J. Stuart, *J. Appl. Phys.* **104** (2008) 103308.
- [12] C. Pardanaud, G. Giacometti, C. Martin, R. Ruffe, T. Angot, E. Aréou, B. Pégourié, E.

- Tsitrone, T. Dittmar, C. Hopf, W. Jacob, T. Schwarz-Selinger and P. Roubin, accepted in the *Journal of Nuclear Materials*, doi:10.1016/j.jnucmat.2010.09.053.
- [13] C.O. Reinhold, P.S. Krstic, S.J. Stuart, H. Zhang, P.R. Harris, F.W. Meyer, *Journal of Nuclear Materials* **401** (2010) 1.
- [14] D. A. Alman, D. N. Ruzic, *Journal of Nuclear Materials* **313-316** (2003) 182.
- [15] S. J. Stuart, M. Fallet, P. S. Krstic and C. O Reinhold, *Journal of Physics: Conference Series* **194** (2009) 012059.
- [16] S. J. Stuart, A. B. Tutein, J. A. Harrison, *J. Chem. Phys.* **112** (2000) 6472.
- [17] J. F. Ziegler, J. P. Biersack and U. Littmark, "The Stopping and Range of Ions in Solids" (Pergamon, New York, 1985).
- [18] This is achieved by applying the operation $\mathbf{x}' = \Phi \mathbf{x}$, where:
- $$\Phi = \mathbf{I} \cos \theta + \mathbf{e} \otimes \mathbf{e} (1 - \cos \theta) + (\mathbf{I} \times \mathbf{e}) \sin \theta$$
- is the rotation tensor and \mathbf{x} and \mathbf{x}' are the initial and rotated coordinates of the solid. Here \mathbf{I} is the identity tensor and \mathbf{e} is the nominal lattice orientation tensor.
- [19] A. S. Kukushkin, H.D. Pacher, G.W. Pacher, G. Janeschitz, D. Coster, A. Loarte and D. Reiter, *Nuclear Fusion* **43** (2003) 716.
- [20] W.R. Wampler, D.K. Brice and C.W. Magee, *Journal of Nuclear Materials* **102** (1981) 304.
- [21] Z. Zhong, X. Wang, X. Feng, *Journal of Materials Research* **22** (2007) 2770.
- [22] J. W. A. M. Gielen, P. R. M. Kleuskens, M. C. M. van de Sanden, L. J. van Ijendoorn, D. C. Schram, E. H. A. Dekempeneer, and J. Meneve, *J. Appl. Phys.* **80** (1996) 5986.
- [23] R. Haerle, E. Riedo, A. Pasquarello, and A. Baldereschi, *Phys. Rev. B* **65** (2001) 045101
- [24] J. K. Walters, P. J. R. Honeybone, D. W. Huxley, R. J. Newport, and W. S. Howells, *Phys. Rev. B* **50** (1994) 831.
- [25] J. T. Titantah and D. Lamoén, *Carbon* **43** (2005) 1311.
- [26] P. S. Krstic and C. O Reinhold, *Proceedings of the 16th International Conference on Atomic Processes in Plasmas, AIP Conf. Proc.* **1161** (2009) 75.

Figure captions:

Figure 1: Equilibrated atomistic structure at 1000K of the as-prepared graphite target. The target is rotated 60° with respect to the hexagonal basal orientation. Deuterium ions are bombarded into the top surface.

Figure 2: Evolution of the deuterium content in the graphite substrate as a function of the number of bombarded ions (dose). After approximately 3200 impingements ($\approx 4.8 \times 10^{16}$ ions cm⁻²) the D content plateaus, signaling steady state saturation. The absorption efficiency η is also shown as a function of dose. A dashed horizontal line marks the zero efficiency reference.

Figure 3: C-C pair correlation function for the target studied here at the beginning of irradiation and after 3900 impacts (5.8×10^{16} ions cm⁻²). $g_{C-C}(r)$ is normalized to the pure graphite density. The unsaturated *a*-C:D target used in ref. [7] is shown for comparison.

Figure 4: Equilibrated atomistic structure at 1000K after 3900 impacts (5.8×10^{16} ions cm⁻²). C atoms are in gray, D atoms in red.

Figure 5: Total pair correlation function as a function of dose. $g_t(r)$ is normalized to the pure graphite density.

Figure 6: Evolution of the hybridization ratio with dose.